

# Droplet detachment and bead formation in visco-elastic fluids

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The presence of a very small amount of high molecular weight polymer significantly delays the pinch-off singularity of a drop of water falling from a faucet, and leads to the formation of a long-lived cylindrical filament. In this paper we present experiments, numerical simulations, and theory which examines the pinch-off process in the presence of polymers. The numerical simulations are found to be in excellent agreement with experiment. As a test case, we establish the conditions under which a small bead remains on the filament; we find that this is due to the asymmetry induced by the self-similar pinch-off of the droplet.

The pinch-off of liquid drops has attracted considerable attention in recent years [1], not the least owing to its enormous technological applications in biotechnology, micro-scale manufacturing, and spray technology [2, 3, 4]. More recently, the breakup of droplets of visco-elastic liquids has been studied both experimentally and theoretically. The interest of considering visco-elasticity is both fundamental and applied. From the fundamental side, the addition of minute amounts of polymers has been shown to inhibit the finite-time singularity that happens at breakup. From the applied side, in many applications, such as fire fighting, inkjet printing, or pesticide deposition on plant leaves, complex fluids have been used to control or modify drop sizes.

For drop detachment in Newtonian fluids, the dynamics is governed by the mathematical properties of the similarity solutions which describe the thinning of the fluid neck. Most importantly for applications, these similarity solutions are always *independent of initial conditions*, and hence it is very difficult to control drop breakup by an external manipulation of parameters. Therefore, the opportunities offered by complex fluids are tremendously important.

In this Letter, we consider the detachment process in the simplest possible visco-elastic case, that of a dilute aqueous solution of flexible polymers. The detachment is studied experimentally for a well-characterized polymer. This allows us to use a model for the elasticity due to the introduction of the polymers, and perform numerical simulations of the detachment process. The good agreement between experiment and numerics permits to study the detachment process in great detail. As a test case, we investigate the condition under which the so-called “beads on a string” structure forms [5], shown in Fig.1a. This intriguing structure is ubiquitous in complex fluids, having been observed for solutions of both flexible and

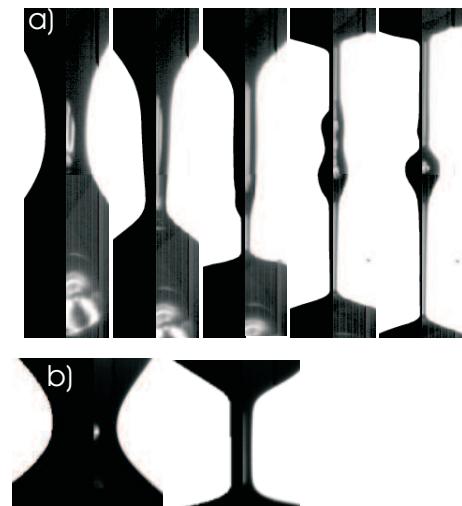


FIG. 1: The droplet detachment process of an aqueous 100ppm PEO solution at different time steps  $t_c - t$  relative to the time  $t_c$  at which the filament is formed. The left half of the pictures are plots from numerical simulations, the right half are experimental photographs : a): nozzle radius  $R = 1.5$  mm (pictures are  $1.2 \times 9$  mm)  $t_c - t = 6, 2, 0, -3, -5$  ms; b:  $R = 0.4$  mm (pictures are  $0.9 \times 0.9$  mm)  $t_c - t = 1, 0$  ms. The model parameters used for the numerical simulation were  $\eta_p = 3.7 \times 10^{-4}$  Pas for the polymeric contribution to the viscosity, a polymer timescale of  $\lambda = 1.2 \times 10^{-2}$ , and an elasticity parameter of  $b = 2.5 \times 10^4$ . The solvent viscosity (water) is  $\eta_s = 1 \times 10^{-3}$  Pas and the surface tension is  $\gamma = 6 \times 10^{-2}$  N/m.

rigid polymers in both low-and high viscosity solvents, and various semi-dilute and concentrated wormlike micellar surfactant solutions. However, depending on the experimental conditions, beads may or may not form.

For the experiments, we focus on the particular case of a drop falling from an orifice (cf. Fig.1), although the theoretical arguments we develop here are more general,

and also apply for instance to filament stretching or filament thinning rheometry. Experiments were performed with aqueous solutions of polyethylenoxide (POE) with a molecular weight of  $4 \times 10^6$  amu, in concentrations of 5 to 2000 ppm. Nozzle radii  $R$  ranged from  $R = 0.25\text{mm}$  to  $R = 5\text{mm}$  and the droplets were generated using a syringe pump in a quasi static mode. Pictures were taken with a high speed camera (1000 frames/s).

We find that the initial stages of the thinning of the liquid column are well described by Rayleigh's linear theory [1], which predicts an exponential growth of the most unstable mode. Thus a growing trough forms on the liquid bridge that separates the falling drop from the tap, whose shape is fairly symmetric around the minimum bridge thickness, as seen in the first panel of Fig.1a and b. In the second panel of Fig.1a the neck shape has already turned asymmetric, while for the smaller pipette radius the shape turns directly to a uniform cylinder. For the asymmetric case, the remaining frames of Fig.1a show how the asymmetric neck structure turns into a secondary bead.

In order to model the detachment, we use the FENE-P (Finite Extensibility Non-linear Elasticity) model [6], a simple polymer model which treats the polymers as Hookean springs of finite extensibility. The springs can be stretched by the flow, leading to elastic stresses due to the entropic elasticity of the polymer chains. To further simplify the description, we use a 1d long-wavelength theory for the fluid motion [1], leading to a coupled set of equations for the local radius  $h(z,t)$  of the fluid column, the mean fluid velocity  $v(z,t)$ , and the radial and axial components of the polymeric stress  $\sigma_r(z,t), \sigma_z(z,t)$ . For the present problem, only the component in the axial direction  $\sigma_z(z,t)$  is of interest, because this is the principal direction of stretching.

The model parameters used in the simulation were taken from the rheological measurements of [7]. To obtain an optimal description, we used a polymer relaxation time  $\lambda = 1.2 \times 10^{-2}\text{s}$ , about 4 times as long as suggested by [7], from steady-state rheological measurements. Our comparison theory/experiment can be seen as a method of determining the timescale relevant for polymer-flow interactions in a highly non-equilibrium situation. Given the considerable simplification inherent in a single-timescale approach, we believe the correspondence in time scales between the rheological method and the value used here to be quite reasonable.

In Fig. 1 experiments are compared to numerical simulations, finding excellent agreement for the two different pipette radii was obtained by adjusting a single parameter, the polymer relaxation time  $\lambda$ . For the larger pipette radius of  $1.5\text{mm}$  a secondary bead is formed (cf. Fig.1 a)), for the smaller radius of  $0.4\text{mm}$  the elastic thread is completely uniform.

Fig. 2a shows a phase diagram for the existence of a bead. We find that for low polymer concentrations

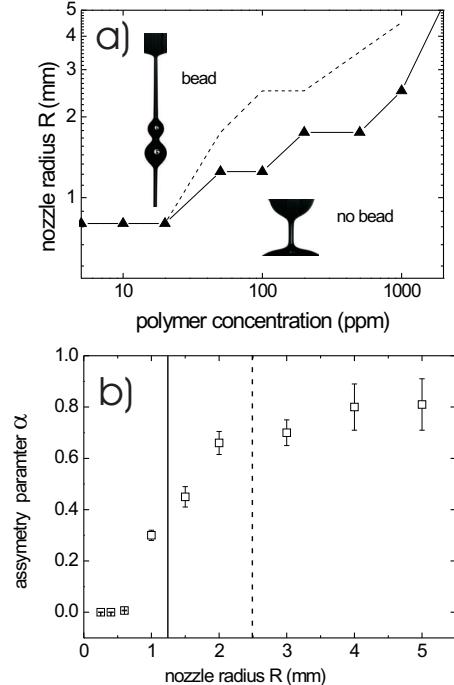


FIG. 2: a) The phase boundary for bead formation, obtained by analyzing experimental runs at polymer concentrations of 5, 10, 20, 50, 100, 200, 500, 1000 and 2000 ppm and nozzle radii  $R = 0.25, 0.75, 1, 1.5, 2, 3, 4, 5\text{mm}$  (triangles). Between the dashed and the full lines a bead is formed, but subsequently disappears. b): The asymmetry parameter  $\alpha$  for the 100 ppm runs measured at  $t_c - t = 1\text{ms}$ . The vertical lines correspond to the transition lines in a).

and large nozzle radius a bead is observed, while in the opposite corner, below the full line, no bead is formed. In the narrow strip between the dashed and the full lines a bead is formed, but is so small that it gets stretched out by elastic stresses and eventually disappears.

From the data shown in Fig.1, it appears that the transition to the asymmetric neck plays an important role for the formation of the secondary bead structure. We quantify the asymmetry using the parameter  $\alpha$  [8]:

$$\alpha = \frac{\int h(z_{\min} + z') - h(z_{\min} - z') dz'}{\int h(z_{\min} + z') + h(z_{\min} - z') - 2h_{\min} dz'}, \quad (1)$$

whose value is zero for a symmetric and one for a staircase profile. The boundaries of integration were chosen at  $h(\pm z') = 2h_{\min}$ . In Fig.2b we show a cut through the phase diagram at constant polymer concentration. Indeed, we find that the asymmetry parameter  $\alpha$  just before onset of the filament undergoes a rather abrupt transition from zero to a nonzero value, exactly at the point corresponding to the boundary between the bead and no-bead regions of Fig.2a in the phase diagram. Similar cuts at constant nozzle radius show the same behavior.

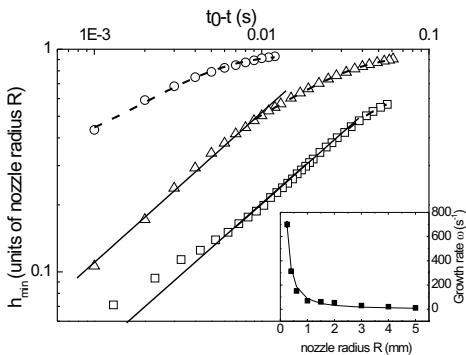


FIG. 3: The minimum neck radius versus time for  $R = 0.4\text{mm}$  (circles),  $R = 1\text{mm}$  (triangles), and  $R = 4\text{mm}$  (squares), at a concentration of  $100\text{ppm}$ , where  $t_0$  is the extrapolated time at which pinch off would take place for a Newtonian liquid. The straight lines are power-law fits yielding an exponent of  $0.66 \pm 0.01$ . The dashed lines are exponential fits to the disturbance amplitude  $1 - h_{\min}/R$ . The squares in the inset are the corresponding growth rates, the line is the theoretical prediction for the most unstable Rayleigh mode of an inviscid fluid.

The transition from the symmetric to the asymmetric shape can be understood by considering the Newtonian motion alone, since the onset of elastic effects is very abrupt for low-viscosity solvents. We confirm this observation by noting that the motion of the minimum neck radius up to just *before* the onset of elastic effects is well described by Newtonian theory, see also [9]. For the regime before the formation of the filament, at early times, the motion is consistent with Rayleigh's theory of exponential growth. More quantitatively, this leads to the growth of the disturbance of the liquid column with a rate  $\omega_R = (0.118\gamma/(\rho R^3))^{1/2}$ , with  $\gamma$  the surface tension and  $\rho$  the liquid density. Corresponding fits to  $h_{\min}$  are shown in Fig. 3 (dashed lines), and compared to theory in the inset. For later times, as the bridge becomes more strongly deformed, the well-known similarity solution [10]  $h_{\min} = 0.7(\gamma(t_0 - t)^2/\rho)^{1/3}$  for the detachment of a low-viscosity droplet takes over. Here  $t_0$  is the extrapolated singularity time, at which the droplet would pinch off in the absence of polymer. This power law corresponds to the straight lines in Fig. 3. We see in Fig. 3 that the power-law behavior is not observed for the smallest nozzle radius: we have not yet transited into the similarity solution regime before the elastic forces due to the polymer intervene and lead to the formation of the filament.

As the Rayleigh theory is a linear stability argument, and the similarity solution is only valid close to the pinch-off, there is no theory for the transition between the two regimes. However experimental observations show that the transition from an asymmetric to a symmetric shape

occurs at a fixed value of  $h_{\min}/R = 0.17 \pm 0.01$ , corresponding to a sufficiently strong deformation of the liquid bridge.

Bead formation can now be understood from the interplay between inviscid dynamics and elastic effects: in regions where significant polymer stretching occurs a uniform thread is formed. If elongation rates during the initial Rayleigh thinning are sufficiently high for the polymers to stretch, the symmetric Rayleigh solution transforms directly in a uniform thread, as shown in Fig. 1b. For larger values of  $R$ , however, the elongation rates are smaller and polymer stretching sets in later, such that the asymmetric similarity solution develops without being influenced by the presence of the polymers.

From Fig. 1a it is evident that the bead starts to form at the bottom of the filament, near the droplet, where the elongation rate becomes very large in this region, a filament forms in a very localized fashion. Meanwhile, the rest of the fluid neck continues to evolve as if the fluid were inviscid, eventually pinching at the top of the neck. As a result, another filament forms, isolating a bead in the middle (cf. Fig. 1a). Thus the bead is the exact analogue of the so-called "satellite drop" [1], which is always formed between the main drop and the faucet in the case of a Newtonian fluid. However, the polymer prevents pinch-off, and a thread remains, connecting the "satellite drop" to both the main drop and the faucet.

If the growth rate  $\omega_R$  of the Rayleigh instability exceeds  $\lambda^{-1}$ , such that polymer stretching takes place from the start, no bead is formed. Thus  $R_{\text{crit}} = (0.118\lambda^2\gamma/\rho)^{1/3} \approx 1\text{mm}$  is the critical radius above which a bead is formed, in good agreement with experiment for low polymer concentrations. The influence of polymer concentration, is relatively minor, in agreement with this argument: the critical radius changes only by a factor of *two* while the concentration varies by two orders of magnitude. The slight increase of  $R_{\text{crit}}$  with concentration reflects an increase in the relaxation time  $\lambda$ , perhaps indicating overlap [11].

The growth of elastic stresses due to the stretching of the polymer, can be calculated as follows. The last stages of the inviscid motion are very fast, so the polymer does not have time to relax. In such a case the axial polymer stress is given by the total *deformation*, leading to  $\sigma_z = \sigma_0/h^4$  [12, 13], in excellent agreement with the results of our numerical simulations. The constant  $\sigma_0 = \eta_p h_0^4/(\rho\lambda)$  [13] is determined by the neck radius  $h_0$  at which the timescale of the flow has become shorter than the polymer timescale  $\lambda$ , where  $\nu_p$  is the polymeric contribution to the viscosity.

For simplicity let us focus on the smallest pipette radii, for which we can estimate that  $h_0 \approx R$ ; equating elastic and surface tension forces, we infer that threads start to form when the minimum radius is  $h_{\text{thread}}/R \approx (\eta_p R/(\lambda\gamma))^{1/3}$ . This means the total deformation the

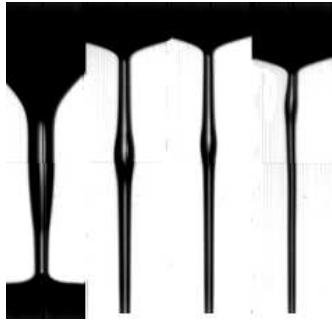


FIG. 4: The migration of the primary bead for the 50ppm,  $R = 1.5\text{mm}$  run (pictures are  $1 \times 4 \text{ mm}$ ). The profiles are shown in time steps of  $2\text{ms}$ . The bead is pushed upward against the direction of gravity.

polymers undergo before a thread forms is proportional to  $\lambda^{-4/3}$ , where  $\lambda$  is proportional to the solvent viscosity, and thus relatively small for water. Our experiments show that the thinning of the filament is exponential, i.e. the elongational rate  $\dot{\epsilon}_0$ , is constant. Exponential thinning of filaments is generally believed [9, 13, 14] to result from a balance of surface tension and elastic forces, concomitant with exponential stretching of polymers.

The present simulations however do *not* agree with this simple picture: by the time filaments are formed, polymer extension is so strong that non-linear effects become important within the present FENE-P modeling. We have chosen the finite extensibility parameter  $b = 2.5 \times 10^4$ , in agreement with [7] and obtain reasonable agreement between the observed thinning rates in the simulation and the experiments. However, in the simulations the thinning rate only remains constant for less than a decade, in disagreement with the experimental observations. Some experimental confirmation of non-linear effects in the constitutive equations is provided for by our finding of a weak dependence of  $\dot{\epsilon}_0$  on the nozzle radius. However, serious questions remain as for the applicability of the FENE model to strongly nonlinear phenomena in dilute polymer solutions ([15]).

After the discussion of secondary bead formation it is worth examining the subsequent evolution of beads, which can be quite varied. Li and Fontelos [16] predict several scenarios of which we found at least three in our experiments: The disappearance of a bead due to stretching, bead migration, and fusion of threads due to differences in the capillary pressure. Bead stretching (between the dashed and full lines in Fig. 2) occurs if the bead is small and the pressure difference between the bead and the surrounding filament is small. Bead mi-

gration usually follows gravity, but smaller beads may be driven upward by pressure forces (cf. Fig. 4), where they fuse with the upper reservoir. Small beads also get sucked into larger ones (cf. Fig. 1a), because their internal pressure is higher.

In conclusion we have measured and described the detachment of a drop of a visco-elastic liquid, and determined the conditions for the formation of a secondary bead in a the detachment process. Our numerical simulations describe the drop formation process in very favorable agreement with the experiments, and allow us explain the qualitative features of the 'phase diagram' for the formation of secondary beads. However, for later times strong non-linear effects become important, and the agreement between experiment and simulation is less good.

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